

# 1 On the unexplained stratospheric ozone losses during cold 2 Arctic Januaries

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9 **Abstract.** Using a combination of data from Match, POAM II,  
10 POAM III and MLS we show that the chemical loss rate of  
11 Arctic O<sub>3</sub> during January of four cold winters (1992, 1995,  
12 1996, and 2000) is consistently faster than can be accounted  
13 for by assuming complete activation of reactive chlorine and  
14 standard reaction kinetics. However, O<sub>3</sub> loss rates measured  
15 during late February and early March 1996 are shown to be  
16 consistent with observations of ClO. The faster than expected  
17 O<sub>3</sub> loss rates during January are shown to occur when air  
18 parcels are illuminated at high solar zenith angles (SZAs  
19 between ~85 and 94°), and to result in cumulative O<sub>3</sub> loss of  
20 ~0.5 ppmv. The cause of the rapid January O<sub>3</sub> loss is unclear,  
21 but may be related to a photolytic process at high SZA that is  
22 poorly represented by current photochemical models.

## 23 1. Introduction

24 Proper understanding of the timing and extent of chemical  
25 depletion of Arctic O<sub>3</sub> during winter is a prerequisite for  
26 developing reliable assessments of future ozone abundances.  
27 Early studies suggested consistency between *observed* rates of  
28 chemical O<sub>3</sub> loss (hereafter referred to as O<sub>3</sub> *loss\_obs*) and  
29 *modeled* loss rates (O<sub>3</sub> *loss\_mdl*) based on measured  
30 concentrations of ClO and BrO and relevant laboratory kinetics  
31 [e.g., Salawitch *et al.*, 1990]. These studies focused primarily  
32 on the February to March time period and were limited by  
33 large (e.g., factor of two) uncertainties in O<sub>3</sub> *loss\_obs*  
34 [Schoeberl *et al.*, 1990].

35 Several recent studies suggest that observed rates of  
36 chemical loss of Arctic O<sub>3</sub> are considerably faster than  
37 expected during mid-winter. Becker *et al.* [1998, 2000]  
38 reported that O<sub>3</sub> *loss\_obs* for mid-January was more than a  
39 factor of two greater than loss rates found using a parcel-  
40 trajectory photochemical model. Hansen *et al.* [1997] reported  
41 that the accumulated O<sub>3</sub> loss observed at 69.3°N in late March  
42 1996 was ~50% larger than values calculated using a chemical  
43 transport model (CTM). A similar discrepancy has been  
44 reported based on analyses of O<sub>3</sub> from the POAM (Polar  
45 Ozone and Aerosol Measurement) II satellite instrument using  
46 a different CTM [Deniel *et al.*, 1998].

47 Using a combination of data from the Match technique,  
48 POAM II, POAM III and the Microwave Limb Sounder

1 (MLS), we show that Arctic ozone loss rates during cold  
 2 Arctic Januaries are consistently faster than is currently  
 3 understood. Our study focuses on O<sub>3</sub> loss rates measured by  
 4 the Match technique [e.g., *Rex et al.*, 1993, 1997, 2002; von  
 5 der Gathen, 1995] for four cold Arctic winters that experienced  
 6 significant chemical ozone depletion during January. We use a  
 7 simple theoretical framework for modeling chemical ozone  
 8 loss rates [*Salawitch et al.*, 1993] that is based on abundances  
 9 of ClO specified either from MLS satellite observations  
 10 [*Santee et al.*, 1996] or by assumptions regarding the level of  
 11 chlorine activation. We investigate the consistency between  
 12 O<sub>3</sub> *loss\_obs* and O<sub>3</sub> *loss\_mdl* for different time periods of Arctic  
 13 winter.

## 14 2. Chemical Loss of Arctic Ozone: January

15 Fig. 1 shows values of O<sub>3</sub> *loss\_obs* on isentropic surfaces of  
 16 the lower stratosphere found by the Match technique for four  
 17 winters. These measurements are based on data collected by  
 18 ozonesondes from dozens of stations in a coordinated manner  
 19 that allows air masses to be sampled multiple times as they  
 20 traverse the vortex [e.g., *Rex et al.*, 1998, 1999]. The loss rates  
 21 are expressed in ppbv/sunlit hour, a convenient way to account  
 22 for variations in solar insolation. The sunlit times are defined  
 23 as periods at solar zenith angles (SZA) less than 95°. The  
 24 discussion in this section focuses on ozone loss rates for  
 25 January of each winter.

26 Chemical loss of O<sub>3</sub> per sunlit hour peaks in January of all  
 27 winters due to greater abundances of ClO [*Rex et al.*, 1997,  
 28 2002]. Data for January 1995 and 2000 are shown for the  
 29 isentropic surfaces that experienced the largest ozone loss rates  
 30 (490 and 500 K respectively). For 1992 and 1996, sufficient  
 31 numbers of ozonesonde observations are not available to  
 32 precisely define loss rates above 475 K. Therefore, for those  
 33 years, ozone loss rates at the 475 K level are given in Fig. 1.

34 As noted above, *Becker et al.* [1998, 2000] could not  
 35 account for the rapidity of ozone loss during January 1992 (at  
 36 475 K) and January 1995 (at 490 K). They used a Lagrangian  
 37 photochemical box model with a comprehensive description of  
 38 gas phase and heterogeneous reactions.

39 To our knowledge, during the cold Arctic Januaries  
 40 discussed here, measurements of ClO at the required altitudes  
 41 are not available, or not sufficiently frequent, to constrain  
 42 model runs along the trajectories used in Match. Therefore we  
 43 have chosen a different approach. To illustrate the extent of the  
 44 discrepancy, we have used a photochemical box model to  
 45 calculate the level of ClO<sub>x</sub> (ClO+2×ClOOCl) that would be  
 46 required to account for the observed O<sub>3</sub> loss rates along Match  
 47 trajectories. In the model we use a simple theoretical  
 48 framework for the representation of the diurnal variation of  
 49 ClO, ClOOCl, OCIO, BrO, BrCl, and atomic O [*Salawitch et al.*  
 50 *et al.*, 1993] (note 1). The calculations assume constant ClO<sub>x</sub>  
 51 along each Match trajectory, account for the effects of  
 52 variations in temperature and solar insolation on O<sub>3</sub> *loss\_mdl*,  
 53 and use kinetic parameters from JPL00-3 [*Sander et al.*, 2000]  
 54 (note 2).

55 The level of ClO<sub>x</sub> necessary to account for the observed  
 56 ozone loss rates in January exceeds 5 ppbv for each winter  
 57 analyzed. This is larger than 3.7 ppbv, the total amount of

1 inorganic chlorine present in the stratosphere [WMO, 1998].  
 2 Ozone loss rates for January found by assuming  $\text{ClO}_x$  equals  
 3 3.7 ppbv are also shown in Fig. 1. The failure to fully account  
 4 for  $\text{O}_3$  *loss\_obs*, even assuming complete activation of  $\text{ClO}_x$ , is  
 5 robust for reasonable uncertainties in the reaction coefficients  
 6 of the primary ozone loss cycles ( $\text{ClO}+\text{ClO}$  and  $\text{BrO}+\text{ClO}$ ).  
 7 These analyses suggest that loss of  $\text{O}_3$  in January occurs by a  
 8 process that is not well represented by current photochemical  
 9 models.

10 The discrepancy between  $\text{O}_3$  *loss\_obs* and  $\text{O}_3$  *loss mdl* is  
 11 significant considering the uncertainty in the measured loss  
 12 rates. The error bars for  $\text{O}_3$  *loss\_obs* in Fig. 1 represent  $1\sigma$   
 13 statistical uncertainties assuming a Gaussian distribution of the  
 14 error of individual Match events (note 3). Observed ozone loss  
 15 rates exceed the maximum possible modeled loss rate  
 16 (assuming  $\text{ClO}_x=3.7$  ppbv) by  $2\sigma$  to  $3\sigma$  for late January 1992  
 17 and by  $1\sigma$  to  $2\sigma$  for parts of mid to late January of other years.

18 The model calculations depend on the abundance of  $\text{BrO}_x$ ,  
 19 the photolysis rate of  $\text{Cl}_2\text{O}_2$  ( $J_{\text{Cl}_2\text{O}_2}$ ) and the reaction rate for the  
 20 reaction  $\text{ClO}+\text{ClO}+\text{M}$  ( $k_{\text{ClO}+\text{ClO}}$ ). To estimate the uncertainty of  
 21 the model results we have varied these parameters within  
 22 reasonable limits, i.e. for  $\text{BrO}$  the highest measurements of  
 23 bromine reported for the Arctic so far (Pfeilsticker et al.,  
 24 private communication) plus 20%, for  $k_{\text{ClO}+\text{ClO}}$  the uncertainty  
 25 given in JPL00-3 (which encompasses the values reported by  
 26 Bloss et al., 2001), and for  $J_{\text{Cl}_2\text{O}_2}$  the recommended value  $\pm$   
 27 50%. The results of some of these sensitivity studies are given  
 28 in Figure 1. For some of the points in January the discrepancy  
 29 is larger than the combined uncertainties of the model results  
 30 and the observations. Our assessment that this discrepancy is  
 31 significant is based also on the consistent observation of faster  
 32 than expected ozone loss rates for all cold Januaries during the  
 33 past decade. However, the uncertainty for  $J_{\text{Cl}_2\text{O}_2}$  given in  
 34 JPL00-3 at 50 hPa is about a factor of three. Using the upper  
 35 limit of  $J_{\text{Cl}_2\text{O}_2}$  based on this uncertainty, all measurements fall  
 36 within the model uncertainty, with the exception of two points  
 37 in January 1992. But increasing  $J_{\text{Cl}_2\text{O}_2}$  by a factor of three  
 38 would not be consistent with analysis of  $\text{ClO}$  measurements at  
 39 high SZA [e.g. Avallone and Toohey, 2001; Vömel et al.,  
 40 2001], which suggest that the 50% used here is a more realistic  
 41 estimate for the uncertainty. Finally, the Match observation of  
 42 essentially zero rates of chemical  $\text{O}_3$  loss for January of warm  
 43 winters (e.g., 1998 and 1999) [Schulz et al., 2001], when  
 44 higher levels of planetary wave activity pose greater challenges  
 45 to the Match approach than for cold winters, increases our  
 46 confidence in the validity of the observed January loss rates  
 47 shown here.

48 A statistical analysis of the ozonesonde data has been  
 49 performed to determine whether sunlight exposure is  
 50 associated with chemical ozone loss. A bivariate linear  
 51 regression has been applied to the data, allowing for different  
 52 rates of ozone change for the sunlit and dark (defined as  $\text{SZA} >$   
 53  $95^\circ$ ) segments of the trajectories [Rex et al., 1999]. Ozone  
 54 depletion, expressed in units of ppbv/hr, is found only for the  
 55 sunlit segments (Fig. 2). No significant change in  $\text{O}_3$  is found  
 56 for the times the airmasses are in complete darkness. The  
 57 consistency of these results for four winters suggests that the  
 58 unaccounted for ozone loss process is photolytic.

1 Since Match results are available for a range of potential  
 2 temperature surfaces, the accumulated loss of ozone can be  
 3 calculated on surfaces that follow the diabatic descend of air  
 4 [Rex *et al.*, 1997]. For 1994/1995 and 1999/2000 the range of  
 5 theta levels for which Match results are available is sufficiently  
 6 broad to do the accumulation on various descending surfaces,  
 7 resulting in a vertical profile of the overall loss at the end of  
 8 January (Fig. 3).

9 Accumulated O<sub>3</sub> loss measured by POAM II and POAM III  
 10 for January 1995, 1996, and 2000, found by allowing vortex  
 11 averaged ozone to descend using calculated cooling rates  
 12 [Hoppel *et al.*, 2002], compares well with Match observations  
 13 considering the respective uncertainties (Fig. 3).

14 Significant chemical removal of O<sub>3</sub> during January has been  
 15 reported by other techniques. Accumulated chemical loss of  
 16 0.5 ppmv of ozone at 465 K was observed by MLS during  
 17 January 1995 (Fig. 3), in excellent quantitative agreement with  
 18 ozone reductions found by Match [Harris *et al.*, 2002].

19 In January 2000 ozone loss derived by Match peaks at  $\sim 0.54$   
 20  $\pm 0.2$  ppmv between potential temperature levels of 480 and  
 21 520 K. Accumulated loss of O<sub>3</sub> was moderate ( $\sim 0.22 \pm 0.13$   
 22 ppmv) at the 444 K surface, close to the cruise altitude of the  
 23 NASA ER-2 aircraft during January. Therefore, the finding of  
 24 little or no chemical loss of ozone ( $0.0 \pm 0.15$  ppmv) from ER-  
 25 2 observations during January 2000 [Richard *et al.*, 2001] is  
 26 not inconsistent with the analyses presented here.

### 27 **3. Chemical Loss of Arctic Ozone: February and** 28 **March**

29 Changes in ozone per sunlit hour are smaller in February  
 30 and March compared to January because of partial recovery of  
 31 ClO<sub>x</sub> to the ClNO<sub>3</sub> reservoir [Rex *et al.*, 1997, 2002]. In this  
 32 section, we use MLS observations of ClO to calculate loss  
 33 rates along the Match trajectories, and compare them to Match  
 34 estimates of O<sub>3</sub> *loss\_obs*.

35 1996 is the only year for which Match observations of rapid  
 36 ozone loss overlapped with sufficiently dense MLS  
 37 observations of ClO to allow the reconstruction of ClO<sub>x</sub> along  
 38 the match trajectories. MLS observations during rapid ozone  
 39 loss in other years were not available due to the monthly yaw  
 40 of the Upper Atmospheric Research Satellite (UARS) or were  
 41 not sufficiently dense due to difficulties with the MLS scan  
 42 mechanism in later years.

43 We have reconstructed the abundance of active chlorine  
 44 along the Match trajectories by interpolating between mixing  
 45 ratios of ClO<sub>x</sub> that have been inferred from MLS  
 46 measurements of ClO close to the respective trajectories. We  
 47 use Version 5 MLS retrievals, which provide a better definition  
 48 of the vertical distribution of ClO than previous MLS retrievals  
 49 [Livesey *et al.*, 2002]. O<sub>3</sub> *loss\_mdl* was calculated along each  
 50 Match trajectory at 475 K for this time period. All other  
 51 assumptions (i.e., BrO<sub>x</sub>, O<sub>3</sub>) are as previously described.<sup>1</sup>

52 Excellent agreement is found between decreases in O<sub>3</sub> along  
 53 the Match trajectories and modeled loss based on MLS  
 54 observations of ClO for late February/early March 1996 (Fig.  
 55 4). The hourly ozone loss rates (e.g., change per sunlit hour)  
 56 are considerably smaller than are observed during January.

1 Abundances of ClO<sub>x</sub> inferred from MLS ClO along Match  
2 trajectories range from ~1.2 to 2.6 ppbv. Most importantly, the  
3 Match trajectories spend a considerably smaller portion of their  
4 overall sunlit time at high SZA (e.g., between ~85 and 94°)  
5 than is found for the January trajectories.

#### 6 **4. Discussion**

7 We turn our attention to speculation regarding the cause of  
8 the rapid ozone loss during January. Standard photochemical  
9 models predict relatively slow rates of polar O<sub>3</sub> loss at high  
10 SZA (e.g., between 85 and 94°) because strong attenuation of  
11 UV light, due to the high O<sub>3</sub> slant columns, limits the  
12 photolysis rate of ClOOCl and hence the overall rate of O<sub>3</sub> loss  
13 by the ClO+ClO and BrO+ClO cycles.

14 Longwave photolysis of ClOOCl by an unknown state in the  
15 near IR (wavelengths > 800 nm, which is optically thin even at  
16 high SZA) could principally provide a strong enhancement to  
17 the abundance of Cl and ClO during twilight. Such photolysis  
18 could lead to significant increases in chemical ozone loss rates  
19 at high SZA. Little change would occur for calculated loss  
20 along trajectories in late February and early March because air  
21 parcels spend a much smaller fraction of overall sunlit time at  
22 high SZA. However, in-situ observations of ClO and ClOOCl,  
23 obtained from the NASA ER-2 during SOLVE, provide  
24 evidence that ClOOCl does not photolyze at an appreciable  
25 rate in the near IR [Avallone and Toohey, 2001; Vömel et al.,  
26 2001; R. M. Stimpfle, private communication, 2002]. Hence,  
27 we are left to ponder other possible causes of the observed  
28 rapid loss of ozone during January.

29 O<sub>3</sub> could also be lost by reactions on the surface of PSCs  
30 (polar stratospheric clouds). The upper limit for the reaction  
31 probability of this process,  $2.5 \times 10^{-4}$  on the surface of nitric acid  
32 trihydrate [Sander *et al.*, 2000], suggests that this process  
33 could contribute significantly to ozone loss in January. For  
34 each January considered here, air was exposed to considerable  
35 amounts of PSCs during both day and night. Our finding that  
36 loss of ozone occurs only during sunlit periods suggests that, if  
37 direct loss on PSC surfaces is responsible, such loss must be  
38 driven by photons.

39 Observations indicate that BrO does not fall off with  
40 increasing SZA near sunset as rapidly as expected [Wahner  
41 and Schiller, 1992; Avallone and Toohey, 2001]. It is difficult  
42 to reconcile these observations with existing photochemical  
43 theory. Nonetheless, it is not clear how enhanced BrO in  
44 twilight could lead to appreciable increases in chemical loss  
45 rates since ClO is observed to decline with increasing SZA  
46 essentially as expected [Vömel et al., 2001; Kreher et al., 2002;  
47 R. M. Stimpfle, private communication, 2002]. A reactive  
48 partner is required for ozone destruction by enhanced levels of  
49 BrO, since the self-reaction of BrO is too slow to contribute  
50 appreciable amounts of ozone loss. Observations of a burst of  
51 ClO [Pierson *et al.*, 1999] and BrO [McKinney *et al.*, 1997] at  
52 high SZA at sunrise also suggest that the halogen chemistry at  
53 high SZA is still not fully understood. Perhaps loosely bound  
54 higher oxides of ClOOCl contribute to the rapid ozone loss  
55 found in January, either by reaction with BrO or in other yet  
56 unidentified ozone loss cycles [Sander *et al.*, 1989]. Better  
57 understanding of the photochemistry of this time period

1 requires more extensive observations at high SZA, and  
 2 appropriate potential temperature levels (e.g., 480 to 520 K), of  
 3 BrO, other radicals, and a variety of chlorine species to test the  
 4 budget and partitioning of halogens in the stratosphere.

## 5 **5. Concluding Remarks**

6 We have analyzed data from Match, POAM II, POAM III  
 7 and MLS to assess our understanding of Arctic ozone loss  
 8 rates. The consistent inability to fully account for observed  
 9 ozone loss rates during cold Arctic Januaries suggests the  
 10 existence of a currently unknown ozone loss mechanism.  
 11 Detailed analyses suggest that this loss process involves a  
 12 photolytic step. The lack of measurable loss during warm  
 13 winters indicates that the process is related to ClO<sub>x</sub>. Observed  
 14 ozone loss later during winter (e.g., mid February to early  
 15 March) is in good quantitative agreement with model results  
 16 based on observed ClO, suggesting that the unknown ozone  
 17 loss mechanism is most important at high SZA and low  
 18 temperatures typical of January conditions.

19 During cold Arctic Januaries we find cumulative ozone loss  
 20 of about 0.5 ppmv. Although our and other analyses point  
 21 toward the existence of a currently unknown ozone loss  
 22 mechanism, its relative impact is modest for winters with  
 23 massive ozone depletion. For such winters, loss of ozone  
 24 predominantly occurs during February and March by known  
 25 catalytic processes (ClO+ClO and ClO+BrO) that operate  
 26 efficiently under conditions of high solar illumination.  
 27 Nonetheless, the January discrepancy demands further  
 28 investigation because reliable assessments of future Arctic  
 29 ozone depletion require a full understanding of all significant  
 30 processes that affect ozone.

31  
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## 41 **Notes**

42 1. Values of BrO are found by specifying the sum, BrO+BrCl, as a  
 43 function of potential temperature such that observed mixing ratios of  
 44 BrO in the Arctic vortex [Avallone *et al.*, 1995] are reproduced.  
 45 Measurements of O<sub>3</sub> from Match are also specified along each  
 46 trajectory.  
 47

48 2. Use of the Bloss *et al.* (2001) rate for ClO+ClO+M rather than the  
 49 JPL00-3 [Sander *et al.*, 2000] rate has essentially no effect on our  
 50 model calculations because a faster rate titrates ClO into ClOOCl.  
 51 Hence, the increase in O<sub>3</sub> loss due to the ClO+ClO cycle is nearly  
 52 balanced by the calculated decrease due to the BrO+ClO cycle.  
 53

54 3. An analysis of the individual errors of the Match events shows that  
 55 the distribution of errors is Gaussian [Rex, 1993]. However, based  
 56 on the sample size, it is hard to exclude a small, non-Gaussian  
 57 component at the far edge (e.g., beyond 2σ) of the distribution. Since  
 58 faster than expected ozone loss rates are observed for all cold

1 Januaries, it is unlikely that the discrepancy discussed in this paper is  
2 due to a statistical fluctuation of the data.

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 17 Figure 1. Chemical loss rate of O<sub>3</sub> ( $O_3$  *loss\_obs*) in the Arctic  
 18 vortex for indicated years and isentropic surfaces based on the  
 19 Match method (red boxes; error bars represent 1 $\sigma$  uncertainty).  
 20 The abundance of ClO<sub>x</sub> necessary to account for  $O_3$  *loss\_obs*  
 21 along each trajectory (green dots; see text) for JPL00-3  
 22 kinetics is also shown. Also shown is an estimate of  $O_3$  *loss\_mdl*  
 23 for January of each year assuming ClO<sub>x</sub>=3.7 ppbv (horizontal  
 24 blue line). The dashed lines show results for assuming BrO<sub>x</sub>  
 25 based on measurements of BrO during winter by Pfeilsticker *et al.*  
 26 (private communication) (run 1). The dotted lines are  
 27 results for increasing these values for BrO<sub>x</sub> by 20% (run 2).  
 28 The dash-dotted line show results for increasing J<sub>Cl2O2</sub> by 50%  
 29 (run 3), and the dash-dot-dotted line is for increasing k<sub>ClO+ClO</sub>  
 30 by 30% (run 4). Run 2 and 3 are the lines farthest from the  
 31 base run, run 4 lies closest to the base run.  
 32

33 Figure 2. Rate of change of ozone along Match trajectories for  
 34 data collected during sunlit conditions (defined as SZA < 95°)  
 35 and during dark periods (SZA > 95°) based on bivariate  
 36 regressions for data collected between 5 and 31 January of  
 37 each year for the set of matches used in Fig. 1. Error bars are  
 38 1 $\sigma$  estimates of the statistical uncertainty. During January 1996  
 39 a much smaller number of ozone soundings have been  
 40 performed compared to the other years shown here and the  
 41 uncertainty of the bivariate analysis is much larger.  
 42

43 Figure 3. Accumulated chemical loss of O<sub>3</sub> versus potential  
 44 temperature for Januaries of 1992 (black), 1995 (red), 1996  
 45 (green), and 2000 (blue). Results from Match analyses are  
 46 shown by solid lines with solid markers. The single open  
 47 marker represents a result from MLS for 1 to 31 January 1995  
 48 [Harris *et al.*, 2002]. The dotted lines represent ozone losses  
 49 derived from POAM II and III measurements. For these an  
 50 ozone versus PV relation was derived from POAM  
 51 measurements made during day 32 ± 2 days. The vortex  
 52 average ozone profile was calculated based on these relations  
 53 at various heights. The ozone loss was then estimated by  
 54 comparing this profile with subsided vortex average profiles  
 55 calculated with the same approach for day 5 ± 2 days. Error  
 56 bars represent 1 $\sigma$  uncertainties.  
 57

58 Fig. 4. The chemical loss of O<sub>3</sub> measured by Match between  
 59 20 February 1996 and 3 March 1996 at 475 K versus the  
 60 amount of sunlight exposure along each Match trajectory (red  
 61 squares) and the computed reduction in O<sub>3</sub> along the same  
 62 Match trajectory based on MLS Version 5 measurements of  
 63 ClO (green crosses). Error bars represent the 1 $\sigma$  sigma  
 64 standard deviation of the measured and modeled changes in  
 65 O<sub>3</sub>.  
 66

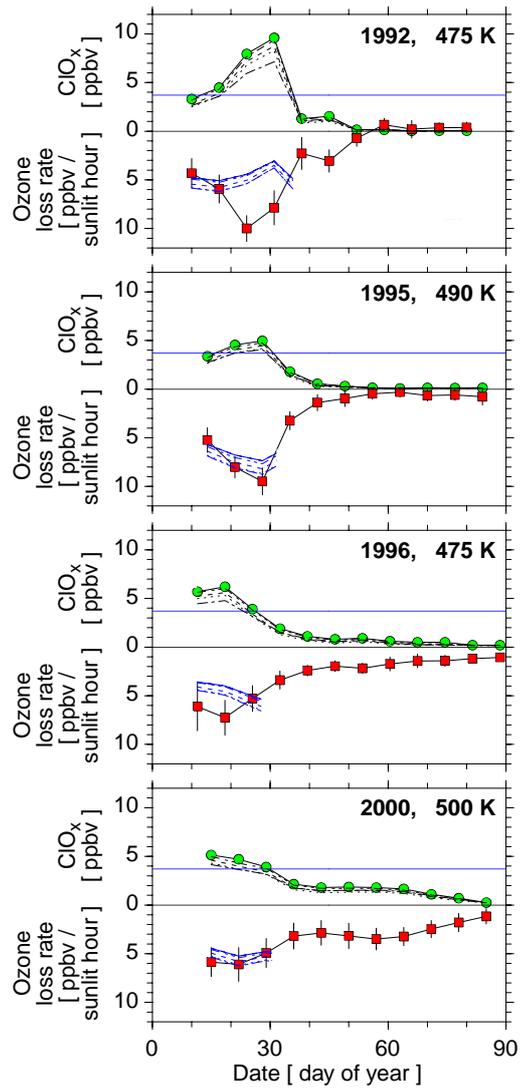


Figure 1, Rex et al.

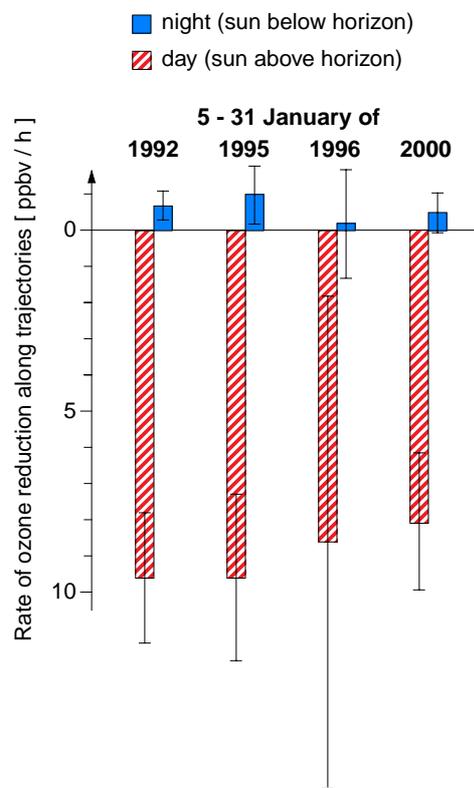


Figure 2, Rex et al.

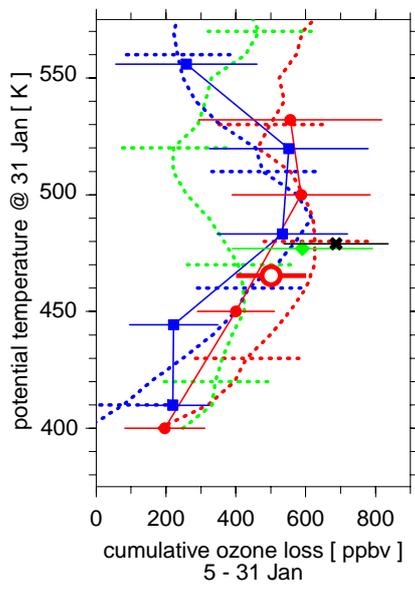


Figure 3, Rex et al.

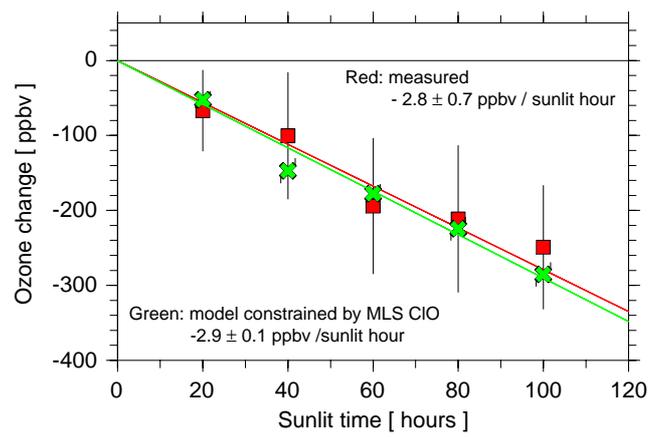


Figure 4, Rex et al.